Effects of Periodic Structure of Opal Matrix as a Photonic Crystal and Solvent on Resonant Raman Scattering and Lasing in Conducting Polymer, Poly(*p*-phenylenevinylene) Derivatives

Katsumi YOSHINO, Yoshiaki KAWAGISHI, Akihiko FUJII and Masanori OZAKI

Department of Electronic Engineering, Graduate School of Engineering, Osaka University
2-1 Yamada-Oka, Suita, Osaka 565-0871, Japan

An intense Raman line is observed upon optical excitation by a second harmonic generation (SHG) light of Nd-YAG laser above some threshold intensity from opals infiltrated with conducting polymer, poly(*p*-phenylenevinylene) derivatives accompanying with spectral narrowing of photoluminescence (PL) by amplified spontaneous emission (ASE) and evolution of multi-mode lasing (ML) lines. The existence of this Raman line is dependent on the solvent used for infiltration. The threshold excitation intensity of the evolution of the Raman line is higher than those of ASE and ML. However, the enhancement of the Raman intensity above the threshold is much more drastic than those of ASE and ML. The results are interpreted in terms of amplification of the resonant Raman line influenced by an optical feedback effect due to the periodic structure of the opal matrix as a photonic crystal.

KEYWORDS: conducting polymer, poly(*p*-phenylenevinylene) (PPV) derivatives, photoluminescence, laser, resonant Raman scattering, opal, photonic crystal

ポリ(*p*-フェニレンビニレン)誘導体の共鳴ラマン散乱及びレーザー発振におけるフォトニック結晶としてのオパールマトリックスの周期構造効果と溶媒効果

吉野　勝美、川岸　義明、藤井　彰彦、尾崎　雅則

大阪大学大学院工学研究科電子工学専攻
〒565-0871 大阪府吹田市山田丘2-1

Nd-YAG レーザーの二倍高調波によるあるしきい値以上の光励起によりポリ(*p*-フェニレンビニレン)誘導体を浸透させたオパールから非常に強いラマン線が観測される。それと共に、自然放出の増幅(ASE)による蛍光のスペクトルナローイングや多モードレーザー発振(ML)が起こる。ラマン線は浸透させる溶媒に依存する。ラマン線が現れるための励起光強度のしきい値は ASE や ML よりも高い。しかしながら、しきい値以上でのラマン強度の増大は ASE や ML よりも顕著である。これはフォトニック結晶としてのオパールマトリックスの周期構造による光学的フィードバック効果に影響される共鳴ラマン散乱の増幅で解釈される。

1. Introduction

Conducting polymers with a highly extended π-electron system in the main chains have attracted much attention from both fundamental scientific and practical technological interests. Especially highly fluorescent conducting polymers such as poly(*p*-phenylenevinylene) (PPV), poly(2,5-dialkoxy-*p*-phenylenevinylene) (ROPPV), poly(3-alkylthiophene), poly(9,9'-dialkylfluorene) have been studied extensively as active materials for electroluminescence (EL) devices. Spectral narrowing and the lasing effect have also been observed in these polymers.[1-4] We have reported laser emission from these conducting polymers in micro-cavity structures upon optical excitation.[5,6]

On the other hand, since the theoretical prediction of a novel concept of a photonic band gap in the photonic crystal with a three-dimensional periodic structure of an optical wavelength order,[7-9] studies on the preparation of such a three-dimensional periodic structure and on their characteristics have been carried out extensively.[10,11] Among various preparation methods, we have reported the preparation of the three-dimensional periodic structure which can also be called as synthetic opal by sedimentation of SiO_2 spheres of several hundreds nm in diameter.[10] We also proposed to realize functionality by infiltration of various materials in the nano-scale space in the opals prepared by this method.[10,11] It has been demonstrated that the opals infiltrated with conducting polymers and fluorescent molecules exhibit spectral narrowing of fluorescence and lasing under optical excitation above some threshold intensity.[12,13]

In this paper, we report observation of the resonant Raman scattering in conducting polymer infiltrated opals upon optical excitation above a threshold intensity and discuss in terms of amplification and lasing in the periodic structures of opal matrix.

2. Experimental

PPV derivatives, poly(2,5-dioctiloxy-*p*-phenylenevinylene) (OOPPV), poly(2,5-dinonyloxy-*p*-phenylenevinylene) (NOPPV), and poly(2-methoxy-5-dodecyloxy-*p*-phenylenevinylene) (MDDOPPV) were prepared by the method already reported.[14,15] These PPV derivatives are soluble in common solvents such as chloroform, toluene, tetrahydrofuran (THF) and pyridine.

By sedimentation of mono-dispersed SiO_2 spheres of several hundred nm diameter (150-500 nm) , a three-dimensional periodic structure with the periodicity of the optical wavelength order was prepared. This can also be called as an opal because of its beautiful opalescent color. Among various opals with three-dimensional periodic structures of SiO_2 spheres of various diameters, here, we mainly use the opal, green opal which was prepared by the spheres of 200-210 nm in diameter. The periodic structure of the opal was inspected by electron-microscope observations utilizing a scanning electron microscope Hitachi S-2000C and by diffraction measurements. Detailed methods was already reported in our previous papers.

Conducting polymers can be infiltrated in the nano-scale interconnected voids in the opal by dipping the opal in conducting polymers in various solvents such as chloroform, toluene, THF and pyridine.

Absorption and photoluminescence (PL) spectra were studied utilizing a HP8452 (Hewlett Packard) and CCD detector PMA-11 (Hamamatsu photonics) , respectively.

Second harmonic generation (SHG) light (532 nm) of Nd-YAG laser (1.06 mm) of 10 ns pulse width was used as an intense optical light source and the emission was measured utilizing a MultiSpec257 spectrograph with a CCD detector (Oriel) having spectral resolution of 0.3 nm.

3. Results and Discussion

Figure 1 shows absorption and PL spectra of MDDOPPV in toluene. In this figure, a reflection spectrum of the green opal (made of SiO_2 spheres of 210 nm diameter) infiltrated with toluene is also indicated. As evident in this figure, a reflection peak is clearly observed and it overlaps with a PL peak in wavelength. The wavelength of SHG is also included in the spectral range of the absorption of MDDOPPV. It should be mentioned that in the case of opals made of SiO_2 spheres of slightly different diameter, the wavelength of the reflection peak shifts slightly, to shorter and longer wavelength with smaller and larger diameters of SiO_2 spheres, respectively. That is, the reflection peak can be tuned by changing diameter of SiO_2 spheres.

Figure 2 (a) shows the emission spectra of the green opal made of SiO_2 spheres of 201 nm in diameter infiltrated with MDDOPPV in THF under various excitation intensities of SHG. At low excitation level, spectrally wide PL was observed at around 590 nm. With increasing excitation intensity, in this case, the PL peak was remarkably enhanced in intensity and spectral width became much narrower accompanying with slight blue shift and sharp emission lines with small separations newly evolved at around 570 nm. The former can be explained by the amplified spontaneous emission (ASE) and the latter by multi-mode lasing (ML) influenced by the optical feed back due to the periodic structure of the opal matrix.[12,13]

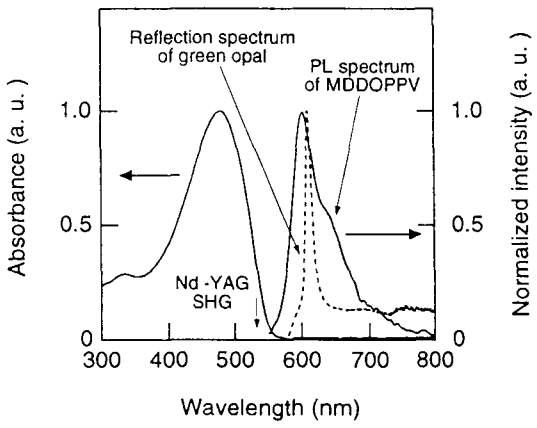

Fig. 1 Absorption and PL spectra of MDDOPPV and a reflection spectrum of a green opal.

図1.MDDOPPVの吸収、PLスペクトル、及びグリーンオパールの反射スペクトル

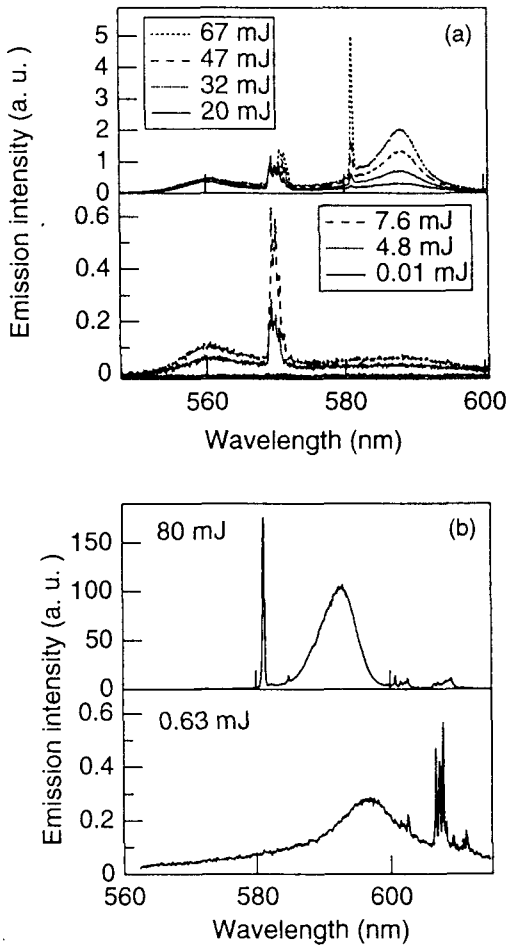

Fig. 2 Emission spectra of MDDOPPV as a function of excitation intensity (a) in a green opal infiltrated with THF and (b) in another green opal infiltrated with toluene.

図2.MDDOPPVの発光スペクトルにおける励起光強度依存性 (a)THFで浸透させたグリーンオパール (b)トルエンで浸透させたグリーンオパール

However, it should be noted in this figure that an extremely sharp line evolves and grows rapidly at 581 nm with increasing excitation intensity above a threshold. The spectral width of the half maximum of this peak is less than the resolution of our detector of 0.3 nm.

In Figure 2(b) emission spectra of MDDOPPV in toluene infiltrated in the other green opal is shown. In this case, the periodicity was about 210 nm and slightly lager than that in Fig. 2(a). In this figure also, ASE and ML were observed under th intense laser excitation. However, in this case ML appeared at slightly longer wavelength than in the case of Fig. 2 (a), because the periodicity of this opal was slightly longer than the case of Fig. 2(a).

It should be noted in this figure, that with increasing excitation intensity further a sharp emission line appeared at 581 nm, which is just the same with the cases of Fig. 2(a). That is, the new line at 581 nm was commonly observed for both cases of opals with slightly different periodicity and therefore this line is interpreted to be originated from MDDOPPV. We have also observed the sharp line at the same wavelength in the green opal infiltrated with NOPPV in toluene and also with OOPPV in THF.

Figure 3 shows the dependences of ASE, ML and the new line intensity at 581 nm on the SHG excitation intensity. As clearly indicated in Fig. 3, the threshold excitation intensity for the appearance of this new sharp line is higher than those of ASE and ML. However, the increase of this new line intensity above the threshold is much more drastic than those of ASE and ML and under high excitation level this new peak becomes dominant in intensity.

On the contrary, in the case of the green opal infiltrated with MDDOPPV in pyridine, such a sharp new line was not observed as shown in Fig. 4.

To understand this anomalous behavior we also studied emission spectra of MDDOPPV solution in

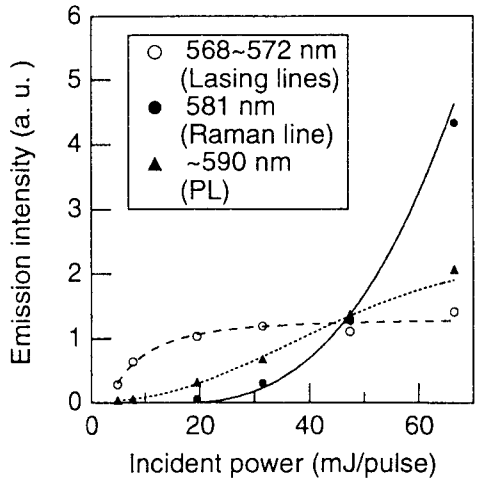

Fig. 3 Dependence of ASE, ML and Raman line intensities of MDDOPPV in a green opal infiltrated with THF on the excitation intensity of Nd-YAG SHG light.

図3.THFで浸透されたグリーンオパールにおけるMDDOPPVのASE、ML、及びRaman散乱のNd-YAG SHG励起光強度依存性

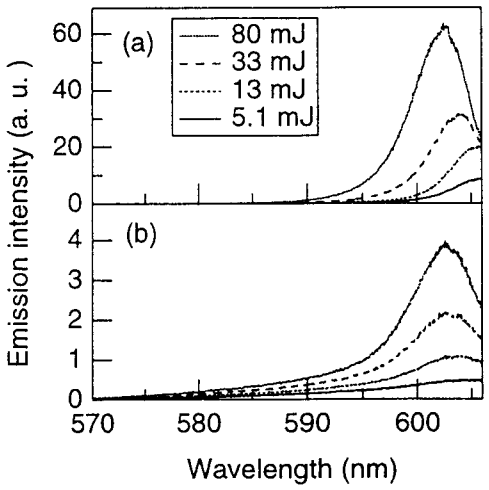

Fig. 4 Emission spectra of MDDOPPV (a) in a green opal infiltrated with pyridine and (b) in pyrydine solution without the green opal.

図4.MDDOPPVの発光スペクトル の励起光強度による変化(a) ピリジンで浸透させたグリーンオパール (b)ピリジン溶液のみ

various organic solvents such as toluene, THF and pyridine without the opal matrix.

In the case of THF solution of MDDOPPV the sharp line at 581 nm also evolved under high excitation intensity. However, its intensity was much lower and the threshold excitation intensity was higher than those of the opal infiltrated with MDDOPPV in THF as evident in Fig. 5. Similar difference in characteristics were also observed between toluene solution of MDDOPPV and the green opal infiltrated with MDDOPPV in toluene. That is, in MDDOPPV in THF without the opal matrix the threshold intensity for the evolution of the line at 581 nm and the intensity of the line above the threshold, were higher and lower, respectively, than those of MDDOPPV in THF infiltrated in the opal matrix.

On the contrary, in the cases of pyridine solution of MDDOPPV and also the opal infiltrated with MDDOPPV in pyridine in which PL peak was located at much longer wavelength compared with the cases of MDDOPPV in other solvents, such a sharp emission peak at 581 nm was not observed even under high excitation intensity as already shown in Fig. 4.

From these experimental results, the origin of this new sharp peak at 581 nm is interpreted to be the resonant Raman line from PPV derivatives.

The difference of photon energy between the primary excitation beam of SHG and this newly evolved line at 581 nm is around 1587 nm^{-1}. It should be mentioned that in Raman scattering spectrum under low excitation intensity, a Raman peak was observed at 1584 cm^{-1}.[16] This Raman line is commonly observed in PPV derivatives.[17]

From these results the sharp line at 581 nm in these figures is reasonable to be attributed to a Raman line. It should be noted in Fig. 4, that the PL peak of MDDOPPV in pyridine solution is located at much longer wavelength than that in THF solution. The absence of the intense Raman line in pyridine solution is due to the small overlap of the Raman line with the PL peak in wavelength. This fact suggests that the line at 581 nm is originated in the resonant Raman effect.

Much enhanced effect of the line of MDDOPPV in the matrix of the opal with the periodicity of the optical wavelength order can be explained by the effect of the optical feedback in the periodic structure of the opal as a photonic crystal.

The existence of the threshold for the evolution an rapid enhancement of the intensity above the threshold may be originated in the amplification effect of resonant Raman line in the periodic structure of opal matrix with the optical feedback in combination with population inversion and lasing.

These results also suggest that the resonant Raman line intensity should become more intense in PPV derivatives which exhibit PL peak at slightly shorter wavelength (nearer to 581 nm) by shortening the conjugation length slightly (for example by degradation), which should also influence on both

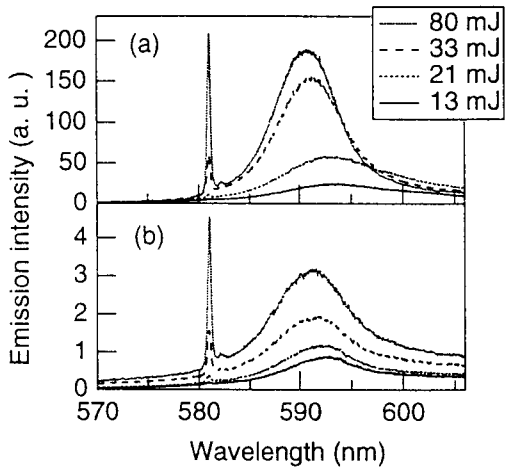

Fig. 5 Emission spectra of MDDOPPV (a) in a green opal infiltrated with THF and (b) in THF solution without the green opal.

図５.MDDOPPVの発光スペクトルの励起光強度による変化 (a)THFで浸透させたグリーンオパール (b)THF溶液のみ

ML and ASE.

4. Summary

The present experimental study can be summarized as follows.

An intense resonant Raman line was observed in the opal infiltrated with ROPPV under optical excitation above the threshold intensity. The existence of the resonant Raman line is dependent on the solvent used for the infiltration. The threshold of this resonant Raman scattering was higher than those of the amplified spontaneous emission (ASE) and the multi-mode lasing (ML). However, the enhancement of the Raman line above the threshold was much drastic compared with those of ASE and ML. The resonant Raman line of ROPPV derivatives in the green opal was much stronger in intensity and the threshold was much lower compared with the case of ROPPV derivatives not in the opal matrix. The results are explained in terms of amplification of the resonant Raman line and lasing influenced by optical feedback due to the periodic nature of the opal matrix as a photonic crystal.

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References

1) N. Tessler, G. J. Denton and R. H. Friend: Nature **382** (1996) 695.
2) S. V. Frolov, M. Ozaki, W. Gellerman, Z. V. Vardeny and K. Yoshino: Jpn. J. Appl. Phys. **35** (1996) L1371.
3) S. V. Frolov, W. Gellerman, M. Ozaki, K. Yoshino and Z. V. Vardeby: Rhys. Rev. Lett. **78** (1997) 729.
4) S. V. Frolov, Z. V. Vardeny and K. Yoshino: Phys. Rev. B **57** (1998) 9141.
5) S. V. Frolov, M. Shkunov, Z. V. Vardeny and K. Yoshino: Phys. Rev. B **56** (1997) R4363.
6) S. V. Frolov, Z. V. Vardeny and K. Yoshino: Appl. Phys. Lett. **72** (1998)1802.
7) E. Yablanovich: Phys. Rev. Lett. **58** (1987) 2059.
8) S. John: Phys. Rev. Lett. **58** (1987) 2486.
9) S. John and T. Quang: Phys. Rev. Lett. **78** (1997) 1888.
10) K. Yoshino, K. Tada, M. Ozaki, A. A. Zakhidov and R. H. Baughman: Jpn. J. Appl. Phys. **36** (1997) L714.
11) K. Yoshino and Y. Kawagishi: J. Soc. Elect. Mat. Eng. **7** (1998) 2.
12) K. Yoshino, S. Tatsuhara, Y. Kawagishi, M. Ozaki, A. A. Zakhidov and Z. V. Vardeny: Jpn. J. Appl. Phys. **37** (1998) L1187.
13) K. Yoshino, S. Tatsuhara, Y. Kawagishi, A. A. Zakhidov and Z. V. Vardeny: Appl. Phys. Lett. **74** (1999) 2590.
14) I. Murase, T. Ohnishi, T. Noguchi and M. Hirooka: Polym. Commun. **28** (1987)229.
15) M. Hamaguchi and K. Yoshino: Jpn. J. Appl. Phys. **33** (1994) L1478.
16) M. Shkunov, W. Gellerman, A. Fujii, K. Yoshino and Z. W. Vardeny: SPIE **3145** (1997) 88.
17) A. Sakamoto, Y. Furukawa and M. Tasumi: J. Phys. Chem. **96** (1992) 1490.

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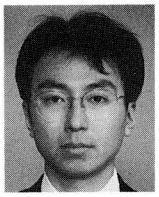
Katsumi Yoshino was born in Shimane, Japan on December 10, 1941. He graduated in 1964 from Department of Electrical Engineering, Faculty of Engineering, Osaka University, where he obtained a Doctor of Engineering Degree in 1969. In that year, he became an Assistant in Electrical Engineering, Osaka University. He promoted to Lecturer in 1972, Associate Professor in 1978. In 1988, he became a Professor in Electronic Engineering, Faculty of Engineering, Osaka University.

Yoshiaki Kawagishi was born in Toyama, Japan on November 29, 1975. He graduated in 1998 from Department of Electronic Engineering, Faculty of Engineering, Osaka University. He is a Master course student of Electronic Engineering in Osaka University.



Akihiko Fujii was born in Osaka, Japan on December 3, 1969. He graduated in 1993 from Department of Electronic Engineering, Faculty of Engineering, Osaka University, where he obtained a Doctor of Engineering Degree in 1997. He was a research fellow of the Japan Society for the Promotion of Science, 1995-1997, and then he became an Assistant in Electronic Engineering, Faculty of Engineering, Osaka University, in 1998.

Masanori Ozaki was born in Aichi, Japan on February 26, 1960. He graduated in 1983 from Department of Electrical Engineering, Faculty of Engineering, Osaka University, where he obtained a Doctor of Engineering Degree in 1988. In that year, he became an Assistant in Electronic Engineering, Osaka University and promoted to Lecturer in 1991. In 1994, he became an Associate Professor in Department of Electronics, Information Systems and Energy Engineering, Osaka University.